

PATENT SPECIFICATION

DRAWINGS ATTACHED

Inventors: ROBERT CHRISTIE BINNING, JOSEPH FLOYD JENNINGS and
EUGENE CHRISTOPHER MARTIN

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COMPLETE SPECIFICATION

Separation Processes

- We, THE STANDARD OIL COMPANY, a Corporation organized and existing under the Laws of the State of Indiana, United States of America, of 910, South Michigan Avenue, Chicago 80, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to separation processes and in particular to processes for separating components from molecular solutions of liquid mixtures containing at least two different components.
- While the separation of mixtures of different molecules has heretofore been effected by employing permeation processes, the prior art leaves much to be desired from the standpoint of developing this technique from a laboratory curiosity to a practicable commercial operation. Numerous disadvantages such as low permeation rates, poor and changing selectivity in the separation, and unsteady operation have hindered development of the process. In addition to these problems, major difficulties arise in starting up and shutting down the permeation process which cause ruptured permeation membranes and/or loss of selectivity of the membrane for permeating one of the components of the mixture to be separated in preference to other components of the mixture. Thus a method which provides trouble-free startup and shutdown techniques and enables operation of the permeation process at high rates of permeation and with good selectivity is vital to the design of a commercial process.
- According to the present invention there is provided a process for separating components from molecular solutions of liquid mixtures containing at least two different components, the molecules of which components have differing solubilities within a plastic membrane which separates a feed zone and a permeate zone of a permeation apparatus, which process comprises starting up the permeation by introducing the mixture into the feed zone of the permeation apparatus under conditions which prevent the membrane being ruptured or losing selectivity maintaining the mixture in the liquid state in the feed zone, permeating a portion of the liquid mixture in the feed zone through the plastic membrane into the permeate zone, maintaining permeation operating temperature which is above the softening point transition temperature as hereinafter defined displayed by the membrane when in contact with the liquid mixture in the feed zone but not higher than 20°C. above the first order transition temperature as hereinafter defined displayed by the membrane when in contact with the liquid mixture in the feed zone, maintaining the permeated portion in the vapour state within the permeate zone, maintaining the absolute pressure in the permeate zone at less than one-half the vapour pressure normally exerted by the permeated portion at the permeation operating temperature, and continuously removing from the permeate zone a vaporised permeated portion which is enriched in the component of the liquid mixture whose molecules are most soluble in the membrane.
- Preferably the absolute pressure maintained in the permeate zone is between 5 and 50 mm Hg.
- The present invention is in part based upon the discovery that many beneficial effects are obtained by carrying out the permeation process where the following condi-

tions simultaneously occur: (1) the permeation temperature is maintained between the softening point transition temperature and not higher than 20°C. above the first order transition temperature displayed by the plastic membrane during its use in the permeation process; (2) the mixture of molecules in the feed zone is maintained in the liquid state; (3) the mixture of molecules in the permeate zone is maintained in the vapour state; and (4) the absolute pressure in the permeate zone is maintained at less than one-half (e.g. one-tenth) of the vapour pressure normally exerted by the mixture in the permeate zone. Among the benefits are a high rate of permeation and a high degree of selectivity. The use of permeation operating temperatures above or below the defined limits results in rupture of the permeation membrane and great reduction in permeation rates, respectively. By maintaining the absolute pressure in the permeate zone under the defined conditions, a great improvement in selectivity is noted.

In the operation of the permeation process, the permeation membrane frequently ruptures at the beginning of the run. This difficulty can be avoided and the permeation process operated at an even higher temperature than heretofore believed possible by special start-up techniques, which may be carried out in the following manner. The process is started up by reducing the absolute pressure in the permeate zone to less than one-half the vapour pressure which the permeated portion normally exerts at the permeation operating temperature prior to contacting the liquid mixture in the feed zone with the plastic membrane at the permeation operating temperature. The liquid feed mixture is then allowed to come into contact with the membrane at a temperature above the softening point transition temperature but not higher than 20°C. above the first order transition temperature displayed by plastic membrane when in contact with the liquid mixture in the feed zone under permeation conditions. For example, the absolute pressure in the permeate zone reduced to 5 to 50 mm. Hg. abs. and thereafter the liquid feed mixture (at a temperature between the softening point transition temperature and not higher than 20°C. above the first order transition temperature displayed by the membrane when in contact with the liquid feed) is introduced into the feed zone. Alternatively, the permeation process can be started up with the liquid feed mixture in contact with the membrane at a temperature below the softening point transition temperature of the membrane, followed by reducing the absolute pressure in the permeate zone to less than one-half the vapour pressure of the permeated portion at the temperature of operation, and then increasing the permeation operating

temperature to above the softening point transition temperature but not more than 20°C. above the first order transition temperature of the membrane.

The permeation process is terminated by reducing the operating temperature to below the first order transition temperature (preferably below the softening point transition temperature of the membrane) and thereafter increasing the absolute pressure in the permeate zone to above one-half the vapour pressure exerted by the permeated portion but not above the pressure on the charge side of the membrane, e.g. increasing the pressure up to atmospheric when the charge is at atmospheric pressure or above. By using this shutdown technique, the selectivity of the membrane is not reduced, i.e. the permeation unit can be put on stream again and the membrane will have the same degree of selectivity; and the chances of rupturing the membrane when the permeation run is started up again is almost negligible.

The selectivity of the permeation membrane (for permeating one molecule more rapidly than other molecules contained in the mixture) can be increased by certain techniques. For example when a permeation run is shut down in a manner not in accordance with the techniques set forth about, the selectivity of the membrane is frequently reduced. Before starting another run to separate the same feed mixture, it is possible to regenerate a substantial part of the membrane's lost selectivity by carrying out a permeation run (using a liquid feed and maintaining the permeated portion in the vapour state while employing operating temperatures above the softening point transition temperature and not higher than 20°C. above the first order transition temperature displayed by the membrane when in contact with the liquid feed) in which the feed is only that most rapidly permeating component of the feed mixture which is to be subsequently separated. The permeation with this particular feed is carried out for a time sufficient to result in the desired increase in selectivity.

The invention will be more readily understood from the following detailed description of an example thereof read in conjunction with the accompanying drawings which form a part of this specification. Figure 1 shows in schematic form a simplified process design for carrying out the separation of high purity benzene from a hydrocarbon mixture containing about 50 per cent benzene. For the sake of clarity many minor equipment items, such as would be apparent to one skilled in this art, have been omitted from the design. Figure 2 sets out in detail the composition and amounts of the various hydrocarbon streams which exist in carrying out the process shown in Figure 1. Figure 3 is a cross sectional view of a portion of the permeation

apparatus such as may be employed in the permeation process of this invention.

Referring now to Figure 1, a benzene fraction containing about 50 per cent benzene with the remainder being close boiling hydrocarbons e.g. methyl cyclopentane, cyclohexane, isoheptanes, (such as might be obtained by the close fractionation of a virgin petroleum naphtha, cracked naphtha, or a catalytically reformed naphtha) is passed from source 11 by way of line 12 to pump 13 and then by way of line 14 to heater 15. The liquid is removed from the heater 15 at a pressure of about 5 p.s.i.g. and a temperature of 90°C. and then passed by way of line 16 into the first permeation stage. The liquid feed to each subsequent permeation stage is under a pressure of 5 p.s.i.g. or higher.

Before any of the liquid mixture is introduced into the first permeation stage, the pumping system connected to the permeate zones of the various permeation stages is activated. Thus the permeate zones in the first permeation stage are evacuated through the permeate exit lines which are connected to permeate manifolding line 17 and then to evacuator-compressor means 18. An absolute pressure of about 50 mm. Hg. is initiated and maintained in the permeate zones of the first and all subsequent permeation stages. Evacuator-compressor 18 is connected by way of line 19 to condenser 20 wherein the permeate is liquified. The compressor section of evacuator-compressor 18 compresses the permeate vapours to a pressure such that they liquify at the permeation operating temperature to be employed in the next permeation stage. The evacuator-compressor means and condensers associated with the subsequent permeation stages are also activated, thereby maintaining a pressure in the permeate zones of the subsequent permeation stages of about 50 mm. Hg. abs. It is to be understood that startup techniques wherein the liquid mixture to be separated is contacted with the membrane prior to reducing the pressure in the permeate zone can be employed. However, it is absolutely essential that the temperature of the liquid mixture contacting the membrane is below the permeation operating temperature (and preferably below the softening point transition temperature of the membrane) if the absolute pressure in the permeate zone has not yet been reduced to less than one-half the vapour pressure exerted by the permeated portion at the permeation operating temperature. For example, alternative startup techniques in which the liquid mixture is introduced into the feed zone at a temperature below the softening point transition temperature of the membrane, followed by reducing the absolute pressure in the permeate zone to that defined, and then increasing the

temperature to the permeation operating temperature, can be used.

The startup techniques described above have been found to be essential in order to operate the permeation process, while using a liquid feed mixture and employing the defined permeation temperatures, at high permeation rates without rupturing the membrane during the start up of the run. The feed mixture to be separated must be contacted while in the liquid state with the permeation membrane in order to obtain the higher permeation rates resulting therefrom. Maintaining the feed mixture in the liquid state during the permeation run enables permeation rates more than 50 percent greater than if the feed were maintained in the vapour state when contacted with the membrane. Startup techniques other than those described by this invention cause rupturing of the membrane. For instance if the permeation process is started up by introducing the feed mixture in the liquid state into the feed zone where it contacts the membrane at a temperature above the softening point transition temperature and especially near the first order transition temperature of the plastic membrane (without previously having reduced the pressure in the permeate zone), and thereafter the pressure in the permeate zone is reduced to bring the permeation process on stream, the membrane will either have a reduced selectivity or it will rupture. Numerous startup tests have substantiated this.

The following Examples illustrate the invention apart from Example 1 which is a comparative example.

EXAMPLE I

A liquid mixture of 55 vol. % acetone-45 vol. % carbon disulphide was charged to the feed zone of a permeation apparatus employing a cellulose triacetate membrane. The feed mixture was at 23°C. the pressure in the feed zone was atmospheric and the pressure in the permeate zone was 760 mm. Hg. abs. As the pressure was reduced in the permeate zone to start up the permeation run, the membrane ruptured immediately.

EXAMPLE II

The permeation startup technique of Example I was repeated except that a pressure of about 40 mm. Hg. abs. was maintained in the permeate zone prior to the time that the feed mixture was introduced into the feed zone of the permeation apparatus. Satisfactory startup and continued operation of the permeation process occurred. In fact the permeation temperature was raised to 40°C. and satisfactory operation occurred at this higher temperature. This results in permeation rates more than twice as great as would occur at the lower temperature of

- 23°C. used in Example I. Thus this startup technique not only prevents rupturing of the membrane but it also permits operation at higher temperatures with consequent higher permeation rates than heretofore believed possible.
- This permeation run is carried out while maintaining an operating temperature between the softening point transition temperature and not higher than 20°C. above the first order transition temperature of the membrane. Transition temperatures are recognised in the prior art as being the temperatures at which plastic materials undergo some change in state which affects decisively certain properties of the plastic e.g. modules of elasticity, thermal conductivity, or electrical resistivity. The softening point transition temperature (frequently coincides with second order or glass transition temperature) occurs at a lower temperature than does the first order transition temperature. The second order (softening point) and first order transition temperatures, although frequently referred to as being fixed and also being independent of the surrounding atmosphere, are in fact greatly affected by the atmosphere in which the plastic material is placed. In general, these transition temperatures are lowered when the plastic is immersed in the liquid feed mixture which is to be separated by permeation. It is to be understood that whenever the terms "softening point transition temperature", "second order transition temperature", and "first order transition temperature" are used they refer to these temperatures displayed by the plastic membrane when the plastic membrane is in contact with the liquid mixture with which it will be in contact during the permeation process. While the transition temperature change depending upon the particular mixture in which the plastic is immersed, they are important factors in the operation of the permeation process. This is because a permeation run which is carried out at a temperature above the softening point transition temperature of the membrane results in higher permeation rates, presumably due to the fact that the molecular segments of the membrane are more mobile and permit more rapid movement of the permeating molecules therethrough. However, the permeation operating temperature should not be more than 20°C. higher than the first order transition temperature of the plastic membrane because at higher temperatures it is thought that the molecular structure of the plastic material becomes so activated that it is readily disintegrated or ruptured. If the defined startup technique of this invention were not employed, it would not be possible to operate at a temperature even as high as the first order transition temperature. By using a startup technique of this invention,
- temperatures up to 20°C. in excess of the first order transition temperature of the membrane can be used. This point up to the interdependence of the startup technique and the carrying out of the permeation run.
- A relatively easy method for determining the softening point transition temperature and the first order transition temperature of any membrane will now be described. A sample of the membrane approximately one mil in thickness, 0.5 inches in width, and approximately 1½ inches in length has clamps approximately one-half inch in size attached to the opposite long ends of the membrane sample. The clamps are attached so as to leave a length of membrane sample approximately one inch long exposed between the two clamps. A weight is attached to the clamp at the lower end of the sample so that the added weight plus the weight of the clamp equal one gram. A sample (at room temperature) of the feed mixture to be permeated is placed in a graduated cylinder or other container provided with a linear scale and a transparent observation window. The sample of the membrane is then suspended from its non-weighted end within the graduated cylinder, so that the membrane sample is totally immersed in the liquid feed mixture. The mixture is then heated at a rate of about 1°C. per minute and the amount of elongation is read directly from the linear scale. The elongation is then plotted against temperature, for example, elongation being plotted as the abscissa and temperature plotted as the ordinate. From numerous plots of elongation versus temperature, it is noted that an almost direct relationship exists between elongation and temperature until the softening point transition temperature of the membrane is reached. Thus the line connecting the points plotting elongation at the various temperatures is essentially a straight line until the softening point transition temperature is reached. With certain membrane compositions and certain feed stock mixtures there is essentially no change in elongation with increase in temperature below the softening point transition temperature of the membrane, whereas with other membrane compositions or feed mixtures there is a gradual but essentially straight line increase in elongation with increase in temperature. The softening point transition temperature is reached before elongation exceeds about 20 per cent (usually 10 percent or less). When the softening point transition temperature is reached, there is an abrupt change in the direction of the line which connects the points plotting elongation at higher temperatures. Frequently this line above the softening point transition temperature is curved and reflects increasingly greater changes in elongation as the temperature is increased. As the temperature is increased even further

- above the softening point transition temperature, the elongation increases until the membrane tears or otherwise disintegrates (usually after elongation of approximately 75 to 150 per cent has been attained). The temperature at which the membrane sample tears is designated herein as the first order softening point transition temperature. Whenever the terms softening point transition temperature and first order transition temperature are referred to herein, it is to be understood that such temperatures are those measured in accordance with the test procedure described in the preceding tests.
- The permeation run is carried out while maintaining the permeate zone at an absolute pressure which is less than about one-half, e.g. one-tenth, of the vapour pressure which the permeated portion normally exerts under the permeation operating temperature. As an example, when the pressure in the feed zone is atmospheric pressure or higher, the absolute pressure in the permeate zone may suitably be between 5 and 50 mm Hg. abs. If the pressure in the feed zone, is, for example 50 p.s.i.g. then the pressure in the permeate zone may be atmospheric pressure. By employing such conditions of reduced absolute pressure in the permeate zone, it is possible to obtain increases in the selectivity of the permeation process of as much as 50 per cent or more while still maintaining the same permeation rates. Selectivity is extremely important in the permeation process, for minor increases in selectivity may reduce the number of stages required in the permeation process and hence cause an astounding reduction in capital investment. Many tests using many different feed stocks and many different plastic membranes verified the beneficial importance of employing the defined reduced pressures in the permeate zone. The following examples illustrate this:
- EXAMPLE III**
- A feed stock containing 39% methanol and 61% benzene was charged in the liquid state at 59°C. to a permeation apparatus using an irradiated polyethylene membrane. The permeate was removed in the vapour state from the permeate zone. When the pressure in the permeate zone was held at 200 mm. Hg. abs. (as contrasted with the ideal vapour pressure of 445 mm. Hg. abs. which normally would be exerted by the permeating portion) the permeated portion at 59°C consisted of 88% benzene and 12% methanol.
- EXAMPLE IV**
- When the same permeation experiment was carried out except that the absolute pressure in the permeate zone was approximately 10 per cent of the ideal vapour pressure that normally would be exerted by the permeated portion, the composition of the permeated portion was 91 percent benzene and 9 percent methanol. In this experiment the absolute pressure in the permeate zone was maintained at about 40 mm. Hg. abs., whereas the ideal vapour pressure which normally would be exerted by the permeated portion was 435 mm. Hg. abs.
- EXAMPLE V**
- The experiment described in Example III was repeated except that the absolute pressure maintained in the permeate zone was equal to the ideal vapour pressure exerted by the permeated portion. In this run the pressure in the permeate zone was about 505 mm. Hg. abs. and the ideal vapour pressure exerted by the permeated portion at the operating temperature was 505 mm. Hg. abs. The composition of the permeated portion was 67 percent benzene and 33 per cent methanol.
- It is apparent from a comparison of Examples III and IV with Example V, that the selectivity of the permeation process can be tremendously increased. Various other membrane compositions and various other molecular mixtures were permeated there-through and similar advantages were noted when the defined low absolute pressures in the permeate zone were employed. For instance when the same feed stock as used in Examples III—V was permeated through a cellulose triacetate membrane at an absolute pressure in the permeate zone equal to the vapour pressure normally exerted by the permeating mixture, the composition of the permeating mixture was 45 per cent methanol and 55 per cent benzene. When the absolute pressure in the permeate zone was about 0.1 of the vapour pressure normally exerted by the permeating mixture, the concentration of methanol in the permeate was increased to 65 per cent methanol, an increase of about 50 per cent.
- Referring again to Figure I, a portion of the feed mixture is permeated through the plastic membrane which separates the feed zone from the permeate zone. Herein, a cellulose acetate butyrate membrane having an acetyl content of 7.4 per cent by weight, a butyryl content of 37.1 per cent by weight, and a free hydroxyl content of 7.3 per cent by weight and being 0.5 mils in thickness is used in all of the permeation stages. The permeation portion is withdrawn from the first permeation stage as a vapour. The vapours pass by way of line 17, through evacuator-compressor 18, then by way of line 19 to condenser 20 in which they are condensed to a liquid. The liquid is then passed by way of line 21 to accumulator 22 and thence by line 23 to pump 24. The permeated portion constitutes about 50 per cent of the feed mixture introduced into the first permeation stage. The permeate from this permeation stage has a composition of

- approximately 77 per cent benzene and 23 per cent of the other hydrocarbons (e.g. heptanes and cyclohexane). The liquid mixture is passed through pump 24 by way of line 25 into the second permeation stage in which the benzene is further concentrated. The liquid feed mixture is at a somewhat lower temperature (for example, about 65—70°C.) in this permeation stage because the softening point and first order transition temperature of the membrane when employed in the permeation process are lower, due to the higher concentration of benzene in the liquid feed to the second stage than existed in the first permeation stage. Except for the temperature, the operation of the second and third permeation stages for benzene purification are essentially the same as the operation of the first permeation stage as was described previously.
- The non-permeated portion, which may comprise about 35 percent of the feed introduced by way of line 25, is removed from the second permeation stage by way of lines 26 and then passed into manifold line 27. This non-permeated portion is a liquid and has a composition comprising about 50 per cent benzene and 50 per cent of other close boiling hydrocarbons e.g. heptanes and cyclohexane. Since it has a composition approximately the composition of the original feed mixture, it is passed by way of line 27 into accumulator 28 from which it is returned by way of line 29 to line 12 and subsequently introduced into the first permeation stage.
- The permeated portion, which comprises about 65 per cent of the feed introduced by line 25 in the second permeation stages for benzene purification, consists of about 93 per cent benzene and 7 per cent of the other close boiling hydrocarbons e.g. heptanes and cyclohexane. The vapours of the permeated portion from the second permeation stage for benzene purification are withdrawn by way of line 30 through evacuator-compressor 31. The compressed vapours are then passed by way of line 32 into condenser 33 wherein they are liquefied. The liquid is then passed through line 34, through pump 35, and then by way of line 36 into the third permeation stage for benzene purification. Because of the higher concentration of benzene in this mixture, the third permeation stage for benzene purification is operated at a lower temperature (for example, at about 45—50°C.) than the second permeation stage for benzene purification.
- The non-permeated portion, which may comprise about 25 per cent of the feed introduced by way of line 36, is removed from the third permeation stage for benzene purification by way of lines 46 and then passed into manifold line 47. This non-permeated portion is a liquid and has a composition comprising about 77 per cent benzene and 23 per cent of other close boiling hydrocarbons e.g. heptanes and cyclohexane. Since it has a composition approximating the composition of the feed mixture to the second permeation stage for benzene purification, it is passed by way of line 47 into accumulator 22 from which it is returned along with the permeate from the first permeation stage to the second permeation stage for benzene purification.
- The permeated portion, which comprises about 75 per cent of the feed introduced by line 36 into the third permeation stage for benzene purification, is almost pure (98—99% purity) benzene. It is removed as a vapour from the permeate zone by way of line 37 through evacuator-compressor 38 and then passed by line 39 to means for liquifying and storing the benzene, which means are not shown herein.
- Referring now to the first permeation stage, the liquid non-permeated portion withdrawn therefrom by way of lines 48 is passed into manifold line 49. This non-permeated portion, which comprises about 50 per cent of the original feed mixture has a composition of about 23 per cent benzene, the remainder being other close boiling hydrocarbons e.g. heptane and cyclohexane. It is passed from manifold line 49 as a liquid into heater 50. It is heated therein to a temperature of about 110°C. (compared with a temperature of 90°C. at which permeation was carried out in the first permeation stage.) The higher temperature, with its consequent higher permeation rate, is permissible because the softening point and first order transition temperatures of the membrane are higher due to the lower benzene concentration in the liquid mixture which is in contact with the permeation membranes. The heated liquid is removed from heater 50 and passed by way of line 51 into the second permeation stage for the recovery of residual amounts of benzene. This permeation stage is conducted essentially in the same manner as has been described for the operation of the other permeation stages except for the permeation temperature.
- The permeated portion (which amounts to about 35 per cent of the liquid charged by way of line 51) is removed from the permeate zone by way of line 52 as a vaporous composition containing about 50 per cent benzene and 50 per cent of the other close boiling hydrocarbons. The permeated portion in line 52 is drawn through evacuator-compressor 53 (which maintains an absolute pressure of 50 mm. Hg. in the permeate zone), the compressed vapours being passed by way of line 54 to condenser 55 wherein they are condensed to a liquid. The liquid is passed by way of line 56 into accumulator 28 from which it is returned to the first permeation stage by way of line 29. Recycling

is carried out since the composition of this stream approximates the composition of the original feed mixture.

5 The liquid non-permeated portion, which comprises about 65 per cent of the feed introduced to the second permeation stage for residual benzene recovery, has a composition of about 7.5 per cent benzene and 92.5 percent of the other hydrocarbons. It is
10 passed by way of lines 57 as a liquid to manifolding line 58 and thence into heater 59. It is heated therein to a temperature of about 120°C. (compared with a temperature of 110°C. at which permeation was carried
15 out in the second permeation stage for residual benzene recovery.) The higher temperature, with its consequent higher permeation rate, is permissible because the softening point and first order transition
20 temperatures of the membrane are higher due to the lower benzene concentration in the liquid mixture which is in benzene, the remainder being close boiling hydrocarbons e.g. n-hexane, methyl cyclopentane, cyclohexane and various isomers of heptane.

25 Figure 2 is a schematic flow diagram which illustrates the separation of benzene from a benzene fraction by a permeation process according to the invention.

30 A charge of 2,000 gallons/day of a benzene fraction containing 50% benzene together with associated close boiling hydrocarbons e.g. n-hexane, methyl cyclopentane, cyclohexane and isoheptanes, is passed into the 1st
35 permeation stage. 1718 gallons/day of the 1st stage permeate containing 77% benzene pass into the 2nd permeation stage (Benzene Purification) where the benzene is further purified. The 2nd stage permeated portion
40 (containing 93% benzene) passes at the rate of 1333 gallons/day to the 3rd Permeation Stage (Benzene Purification) while the non-permeate fraction (718 gallons per day and containing 50% benzene) is recycled to the
45 1st permeation stage. The 3rd permeation stage produces a permeated product containing 98% benzene at the rate of 1000 gallons per day. The non-permeated fraction containing 77% benzene is recycled at the rate of
50 333 gallons per day to the 2nd Permeation Stage. The non-permeated portion (containing 23% benzene) from the 1st Permeation Stage is passed at the rate of 1718 gallons per day to the 2nd Permeation (Residual Benzene
55 Recovery) Stage where it is separated into a permeated portion (containing 50% benzene), which is recycled at the rate of 718 gallons/day to the 1st Permeation Stage, and a non-permeated portion (containing 7%
60 benzene) which is passed at the rate of 1333 gallons/day to the 3rd permeation (Residual Benzene Recovery) stage. The 3rd stage produces 1000 gallons per day of hydrocarbons containing only 2% benzene and 333
65 gallons per day of permeated portion contain-

ing 23% benzene which is recycled to the 2nd Residual Benzene Recovery stage.

A cross sectional view of a portion of the permeation apparatus such as is used in the first and subsequent permeation stages is shown in Figure 3. The feed inlet is indicated by passageway 74. This passageway serves as a manifolding which allows the liquid feed mixture to enter the various individual feed zones designated by 75. As the liquid feed mixture enters the various feed zones it comes in contact with plastic membrane 76 and the molecules in the feed mixture which are more soluble in the membrane permeate therethrough more rapidly than those molecules which are less soluble in the permeation membrane. Thus a portion of the feed mixture permeates through the membrane and passes along griddle-design grooves 77 (permeate zone) in the membrane backing plate 78. The membranes are supported away from backing plate 78 by screen 79. The grooves 77 in the surface of membrane backing plate 78 ultimately lead to a withdrawal passage way 80 in the interior of membrane backing plate 78. This withdrawal passage way 80 then connects with permeate manifolding line 17 by which the permeated portions of the feed mixture are withdrawn from the particular permeation stage. The feed mixture in feed zones 75 progresses upwardly through the feed zones, portions of the introduced liquid permeating through plastic membranes 76 as it progresses upwardly, and the remaining amount of the mixture withdrawn from feed zones 75 is termed the non-permeated portion. The non-permeated portion is withdrawn from the top of feed zones 75 by way of lines 48 which connect with manifolding line 49. Manifolding line 49 combines the individual non-permeated portions in the particular permeation stage. Stationary baffles 81 are positioned within feed zones 75 to prevent differences in composition of the mixture between the zone immediately adjacent the membrane and points nearer the centre of feed zones 75. Because plastic membrane 76 which separates feed zones 75 from permeate zones 77 is tightly sealed, no portion of the feed mixture can pass from the feed zones into the permeate zones except by permeating through plastic membrane 76.

In beginning the shutdown of the permeation process, the temperature of the feed mixtures to the various permeation stages are reduced. The mixtures are not heated to the softening point transition temperature of the membranes with which the particular feed compositions come in contact. Thus, referring to Figure 1, the original feed mixture is not heated in heater 15 and the permeation run is continued at ambient temperatures, e.g. 20°—30°C. Likewise heaters 50 and 59 are shut-off and the non-permeated portion from

- the first and second permeation stages are not heated but are passed directly into the permeation stages which recover residual amounts of benzene. Condensers 20, 33, 55, and 64 are allowed to continue to operate until the temperatures of the various liquid stream reach approximately atmospheric temperatures. After the temperature of the liquid mixtures in contact with the membranes has been reduced to below the first order transition temperature and preferably below the softening point transition temperature (herein, the latter) of the membrane, the operation of evacuator-compressors 18, 31, 53 and 62 is terminated. The permeation run is then at an end. Liquid feed is in contact with the plastic membrane in all of the various permeation zones. This prevents drying out of the plastic membrane which drying out ordinarily causes quick rupture of the membranes in subsequent permeation runs. When it is desired to start up the permeation process to separate an additional batch of the mixture, evacuator-compressors 18, 31, 38, 53 and 62 can be started in operation. The start-up operation is then repeated as was previously described.
- The importance of employing the described shutdown technique was demonstrated in numerous tests. These tests showed that unless the temperature of the liquid feed mixture in contact with the permeation membrane is reduced to below the first order transition temperature of the membrane before allowing the pressure in the permeate zone to rise, the membrane will rupture very readily when the permeation process is put back on stream. If the temperature of the liquid mixture is reduced to below the first order transition temperature but is still above the softening point transition temperature when the pressure in the permeate zone is raised to atmospheric pressure, then the membrane will suffer a loss in selectivity and may rupture when brought on stream. Many tests have shown this. For example, a mixture of 25 vol. % methyl ethyl ketone, 37.5 vol. % n-heptane, and 37.5 vol. % isooctane was charged in the liquid state to the feed zone of a permeation process. Permeation was carried out using a cellulose acetate-butyrate permeation membrane at a temperature of 70°C. while employing a pressure of 40 mm. Hg. abs. in the permeate zone. The permeation run was carried out for a suitable length of time. Thereafter it was desired to terminate the run. The pressure in the permeate zone was allowed to rise to 760 mm. Hg. abs. and permeation was discontinued. Approximately an hour later the unit was started up by first reducing the pressure in the permeate zone. As the pressure was reduced therein the membrane ruptured immediately. This same phenomenon was also observed to occur where the temperature is lowered to 10 to 20°C. below the normal operating temperature but is still above the softening point transition temperature of the plastic membrane. Tests showed, however, that when the permeation run was terminated by lowering the permeation temperature to below the softening point transition temperature of the membrane prior to raising the pressure in the permeate zone to atmospheric pressure and then allowing the liquid feed to contact the membrane for an extended time, the membrane did not rupture or suffer a loss in selectivity when the permeation unit was started up again. Because it is desirable to allow liquid to remain in the feed zone in contact with the membrane when the permeation run is shut down, in order to prevent drying out and cracking of the plastic membrane, this can be done in a practicable manner without having the membrane rupture in subsequent runs by using the described shutdown techniques of this invention.
- As was indicated, termination of the permeation run by increasing the absolute pressure in the permeate zone prior to decreasing the permeation temperature will cause a reduction in selectivity of the permeation membrane when the liquid in the feed mixture is thereafter allowed to remain in contact with the membrane at temperatures above the softening point transition temperature of the membrane. The plastic membrane appears to undergo some reorientation of its molecules which causes this loss in selectivity. It has been found that the selectivity of the membrane can be increased and usually restored substantially to its original selectivity by carrying out a permeation run which appears to recondition the membrane, perhaps by reorienting its molecular structure. In the reconditioning process, a conventional permeation run as defined by this invention is carried out except that the feed mixture employed consists substantially only of that component of the mixture (which mixture is to be used as the feed mixture later) which permeates most rapidly. Thus the feed is maintained in the liquid phase and at a temperature above the softening point transition temperature while the permeate is removed as a vapourised product. It may be necessary to employ a somewhat lower temperature in this membrane reconditioning technique than is used in the permeation run on the feed mixture to be separated because the first order transition temperature of the membrane will be lower in contact with the pure component which permeates more rapidly than it is when in contact with the mixture which is to be separated later. The membrane reconditioning run is carried out for a length of time (usually 1 to 5 hours is satisfactory) sufficient to increase the selectivity and preferably to restore the selectivity of the membrane to

substantially what it was originally. The loss in selectivity of the membrane by using improper techniques for shutting down the permeation run, and regeneration of the selectivity of the membrane by the previously described technique were demonstrated repeatedly in a number of runs. One of the test demonstrating those phenomena is reproduced below as an example.

EXAMPLE VI

A 50—50 mixture of n-heptane and isooctane was charged to the feed zone of the permeation apparatus which employed an ethyl cellulose membrane having an ethoxyl content of about 45 per cent by weight. A permeation temperature of 100°C. was used and the permeated portion was removed as a vapour from the permeate zone (permeate zone maintained at subatmospheric pressure). The composition of the initial permeate consisted of 78% n-heptane and 22% isooctane. Thereafter the permeation run was terminated by allowing the pressure in the permeate zone to increase to atmospheric pressure (by shutting off the vacuum pump connected to the permeate zone), and the hot mixture in the feed zone was allowed to remain in contact with the permeation mem-

brane for 24 hours. The mixture in the feed zone was replaced with a fresh 50—50 mixture of n-heptane and isooctane and the permeation unit was started up by first reducing the pressure in the permeate zone and then heating the mixture in the feed zone to 100°C. The composition of the permeate initially recovered was 64% n-heptane and 36% isooctane. Thus the faulty shutdown resulted in a selectivity drop in the membrane of from 78% n-heptane in the permeate down to 64% n-heptane in the permeate.

Thereafter the mixture in the feed zone was removed and pure n-heptane was introduced into the feed zone. The permeation run was then started up again (in the manner stated immediately above) and permeation of the n-heptane was continued for 2.25 hours. The permeation run was then terminated, the n-heptane removed from the feed zone, and a fresh 50—50 mixture of n-heptane and isooctane was charged to the feed zone. The permeation unit was started up in the preceding manner described and it was found that the initial composition of the permeate was 74% n-heptane and 26% isooctane. The selectivities of the membrane in its different conditions is shown in the following table:

	Amount n-heptane in Feed	Condition of Membrane	Amount n-Heptane in Permeate
	50%	New	78%
60	50%	After faulty shutdown	64%
	50%	After regeneration of selectivity	74%

Thus by the membrane selectivity regeneration technique, the selectivity of the membrane was regenerated or restored to a point where the permeate contained 74% n-heptane as against 64% n-heptane in the run employing the membrane of degenerated selectivity. In addition, the membrane which had its selectivity regenerated also had a permeation rate which was about 8% greater than the original membrane.

The loss in selectivity of the membrane can also be avoided by an improvement in the shutdown technique. The particular improvement consists of discontinuing the flow of the mixture to be separated and substituting in its place the component of the feed mixture which permeates most rapidly. This component should be at a temperature lower than the second order transition temperature of the membrane. As this component passes through the permeation system, it cools down the entire system to below the second order transition temperature of the membrane and thereafter the pressure on the permeate zones can be increased. For example, in the process illustrated in the attached figures, the flow of the feed mixture to the first permeation stage can be discontinued and cooled benzene at a temperature of about 10°C. or

preferably lower can be introduced by line 16 into the first permeation stage. The cooled benzene passes, without subsequent reheating, into the later stages of the system and eventually can be recovered from the system by way of lines 39 and 71. After benzene is in all of the various feed zones and when the temperature through the system is at about 10°C., the pressure in the permeate zones can be restored to atmospheric by shutting down the evacuator-compressors associated therewith. At this point the entire system can be shut down and the plastic membrane is in complete contact with liquid benzene in the feed zones of the various permeation stages. Because it is in contact with the component of the mixture intended to be separated and which component permeates most rapidly, the selectivity of the membrane which remains in contact with the liquid benzene is not reduced. Thereafter when it is desired to start up the permeation process, the usual startup procedure can be used, the benzene which passes through the system first can be recovered, and thereafter the benzene feed mixture to be separated can be introduced into the permeation system by way of line 17.

From the description of the startup tech-

nique, the operating technique, and the shut-
 down technique, it is apparent that the afore-
 mentioned techniques are integrated with
 each other and so interrelated that when used
 5 together they provide a unitary permeation
 process which produces results heretofore un-
 obtainable. Thus the particular startup
 technique enables the permeation run to be
 carried out at temperatures above the first
 10 order transition temperatures of the mem-
 brane, and by operating at such temperatures
 while maintaining the defined reduced pres-
 sure in the permeate zone it is possible to
 obtain high permeation rates at increased
 15 selectivity. It is particularly desirable to
 follow the defined shutdown techniques,
 when the permeation run is carried out in the
 defined manner, in order to prevent a loss in
 membrane selectivity or rupture of the mem-
 20 brane when the permeation run is started up
 again. If the selectivity of the membrane
 becomes reduced inadvertently, for example,
 by the use of improper shutdown techniques,
 it may be restored to substantially its original
 25 selectivity by the regeneration technique
 defined.

While the invention has been described in
 terms of an embodiment in which a cellulose
 acetate butyrate membrane is employed and
 30 a mixture of benzene with close boiling
 hydrocarbons is processed to recover purified
 benzene, the particular membrane, employed
 and the feed mixture separated are illustra-
 tive only and do not constitute an essential
 35 feature of the present invention. A wide
 variety of plastic membranes may be
 employed, and a wide variety of liquid or
 liquefiable mixtures of two or more com-
 ponents in molecular solution (as distinct
 40 from suspensions or colloidal solutions, e.g.
 aqueous sugar solutions, aqueous inorganic
 salt solutions and solutions of chlorophyll,
 which are sometime separated by the process
 of dialysis in which the macromolecule, e.g.
 45 sugar is incapable of passing through a
 dialysis membrane) may be separated. Mole-
 cular solutions of oil soluble organic
 chemicals e.g. mixtures of carbon disulphide
 with acetone, benzene with methanol, hexanol
 50 with butyl sulphide, mixtures of hydro-
 carbons e.g. benzene with cyclohexane or
 various isomeric heptanes, various petroleum
 fractions e.g. naphthas which preferably boil
 over a narrow range, e.g. 20°C., can be
 55 separated using plastic membranes e.g. cellu-
 lose acetate butyrate, cellulose propionate,
 ethyl cellulose, propyl cellulose, polyethylene,
 polystyrene, neoprene, or other plastic mem-
 branes in which the oil soluble compounds
 60 are soluble and permeate therethrough. Mix-
 tures of water soluble organic compounds or
 aqueous solutions of water soluble chemicals
 can be separated by permeation through
 various plastic membranes. For example,
 65 aqueous solutions of ethanol, pyridine,

methyl ethyl ketone or formic acid, can be
 permeated to separate the water therefrom
 while employing permeation membranes such
 as cellulose acetate regenerated cellulose,
 polyvinylalcohol, or polyacrylonitrile. Various
 70 mixtures of oil soluble and water soluble
 organic compounds similarly can be separated
 by permeation through various plastic mem-
 branes e.g. ethyl cellulose, cellulose acetate-
 butyrate, regenerated cellulose, and cellulose
 75 acetate. Because the component which is
 more soluble in the membrane also permeates
 through the membrane more rapidly than the
 other components, the choice of the particular
 membrane to be used will determine whether
 80 the permeated portion is enriched in one
 component or a different component of the
 mixture undergoing separation.

Suitable membranes can also be prepared
 by grafting a thin selective membrane upon
 85 the surface of a thicker membrane which is
 not as selective but has a high permeation rate.
 Since the rate of permeation varies directly
 with the thickness of the membrane, grafted
 membranes produced by this method take
 90 advantage of the high selectivity of a film
 which has a low rate of permeation. Irradia-
 tion can be used to strengthen the film by
 cross linking thus enabling the use of higher
 permeation temperatures which give higher
 95 rates of permeation without materially effect-
 ing the selectivity of the membrane.

WHAT WE CLAIM IS:—

1. A process for separating components
 from molecular solutions of liquid mixtures
 100 containing at least two different components,
 the molecules of which components have
 differing solubilities within a plastic mem-
 brane which separates a feed zone and a per-
 meate zone of a permeation apparatus, which
 105 process comprises starting up the permeation
 by introducing the mixture into the feed zone
 of the permeation apparatus under conditions
 which prevent the membrane being ruptured
 or losing selectivity maintaining the mixture
 110 in the liquid state in the feed zone, per-
 meating a portion of the liquid mixture in
 the feed zone through the plastic membrane
 into the permeate zone, maintaining a
 permeation operating temperature which is
 115 above the softening point transition tempera-
 ture as herein defined displayed by the mem-
 brane when in contact with the liquid mixture
 in the feed zone but not higher than 20°C.
 above the first order transition temperature as
 120 herein defined displayed by the membrane
 when in contact with the liquid mixture in
 the feed zone, maintaining the permeated
 portion in the vapour state within the per-
 meate zone, maintaining the absolute pressure
 125 in the permeate zone at less than one-half the
 vapour pressure normally exerted by the
 permeated portion at the permeation
 operating temperature, and continuously re-

moving from the permeate zone a vaporized permeated portion which is enriched in that component of the liquid mixture whose molecules are most soluble in the membrane.

5 2. A process as claimed in claim 1 wherein the absolute pressure maintained in the permeate zone is between 5 and 50 mm. Hg.

3. A process as claimed in claim 1 or claim 2 wherein the permeation process is started up by reducing the absolute pressure in the permeate zone to less than one-half the vapour pressure which the permeated portion normally exerts at the permeation operating temperature prior to contacting the liquid mixture in the feed zone with the plastic membrane at the permeation operating temperature.

4. A process as claimed in claim 1 or claim 2, wherein the permeation process is started up by reducing the absolute pressure in the permeate zone to less than one-half of the vapour pressure which the permeated portion normally exerts at the permeation operating temperature prior to contacting the liquid mixture in the feed zone with the plastic membrane at a temperature which is above the softening point transition temperature displayed by the membrane when in contact with said liquid mixture.

5. A process as claimed in claim 1 or claim 2, wherein the permeation process is started up by a method which comprises the steps of (1) contacting the liquid mixture in the feed zone with the plastic membrane at a temperature below the softening point transition temperature which the membrane displays when in contact with said liquid mixture (2) thereafter reducing the absolute pressure in the permeate zone to less than one-half the vapour pressure which the permeated portion normally exerts at the permeation operating temperature, (3) and then increasing the temperature of the liquid mixture in the feed zone to the permeation operating temperature.

6. A process as claimed in any one of the preceding claims wherein the permeation process is shut down by the steps of (1) lowering the permeation operating temperature to a temperature below the softening point transition temperature displayed by the membrane when in contact with the liquid mixture in the feed zone, and (2) thereafter increasing the pressure in the permeate zone to at least atmospheric pressure but not to a higher pressure than exists in the feed zone.

7. A process as claimed in any one of the preceding claims wherein the permeation membrane has been regenerated by introducing into the feed zone of the permeation apparatus a regenerative feed consisting substantially entirely of that component of the given mixture whose molecules permeate through the membrane more rapidly than the molecules of other components of said given

mixture, permeating the regenerative feed through the membrane into the permeate zone while employing a permeation operating temperature which is above the softening point transition temperature displayed by the membrane when in contact with the regenerative feed but not more than 20°C. above the first order transition temperature displayed by the membrane when in contact with said regenerative feed, maintaining the permeated portion in the permeate zone in the vapour state and continuously removing permeate vapours therefrom, carrying out said permeation until the selectivity of the permeation membrane has been increased.

8. In a permeation process for separating molecular solutions of liquid mixtures containing at least two different components in which process is employed a permeation apparatus comprised of a feed zone and a permeate zone which are separated from each other by a plastic membrane in which molecules of one component of the liquid mixture are more soluble than molecules of another component, the improvement which comprises the steps of: (1) starting up the permeation process by maintaining an absolute pressure in the permeate zone which is less than one-half the vapour pressure which the permeated portion normally exerts at the permeation operating temperature prior to contacting of the liquid mixture in the feed zone with the plastic membrane at the permeation operating temperature, thereafter contacting the liquid mixture with the plastic membrane at the permeation operating temperature, said permeation operating temperature being above the softening point transition temperature displayed by the membrane when in contact with the liquid mixture in the feed zone but not more than 20°C. above the first order transition temperature displayed by the membrane when in contact with the liquid mixture in the feed zone, (2) permeating a portion of the liquid mixture in the feed zone through the plastic membrane into the permeate zone while continuously removing from the permeate zone a vaporized permeated portion which is enriched in that component of the liquid mixture whose molecules are most soluble in the membrane, and (3) shutting down the permeation run by lowering the temperature of the liquid mixture in contact with the plastic membrane to below the softening point transition temperature displayed by the membrane when in contact with the liquid mixture in the feed zone, and subsequently increasing the pressure in the permeate zone to at least atmospheric pressure but not above the pressure which exists in the feed zone.

9. A process for separating molecular solutions of liquid mixtures containing at least two different components as claimed in claim 1, substantially as hereinbefore described

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with reference to and as illustrated in the accompanying drawings.

5 10. A process as claimed in any one of the preceding claims wherein the molecular solution is a liquid mixture containing benzene and close boiling hydrocarbons and the membrane is one in which benzene is the most soluble component of the mixture.

10 11. Components from molecular solutions of liquid mixtures when separated by the pro-

cess claimed in any one of the preceding claims.

12. Benzene whenever separated from molecular solutions containing it by a process as claimed in any one of the claims 1 to 10. 15

BOULT, WADE & TENNANT,
111 & 112, Hatton Gardens, London, E.C.1,
Chartered Patent Agents,
Agents for the Applicant(s).

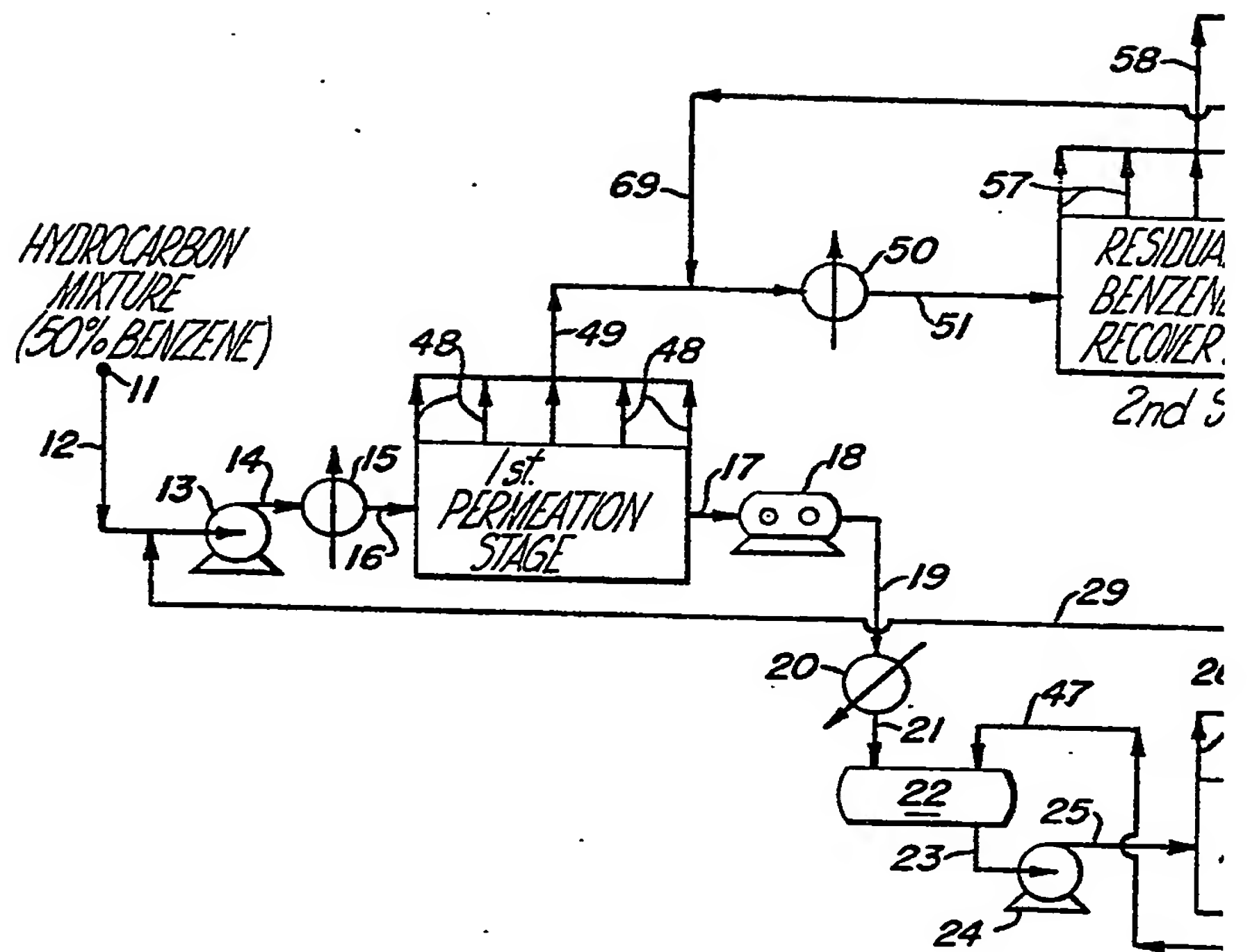


Fig. 1

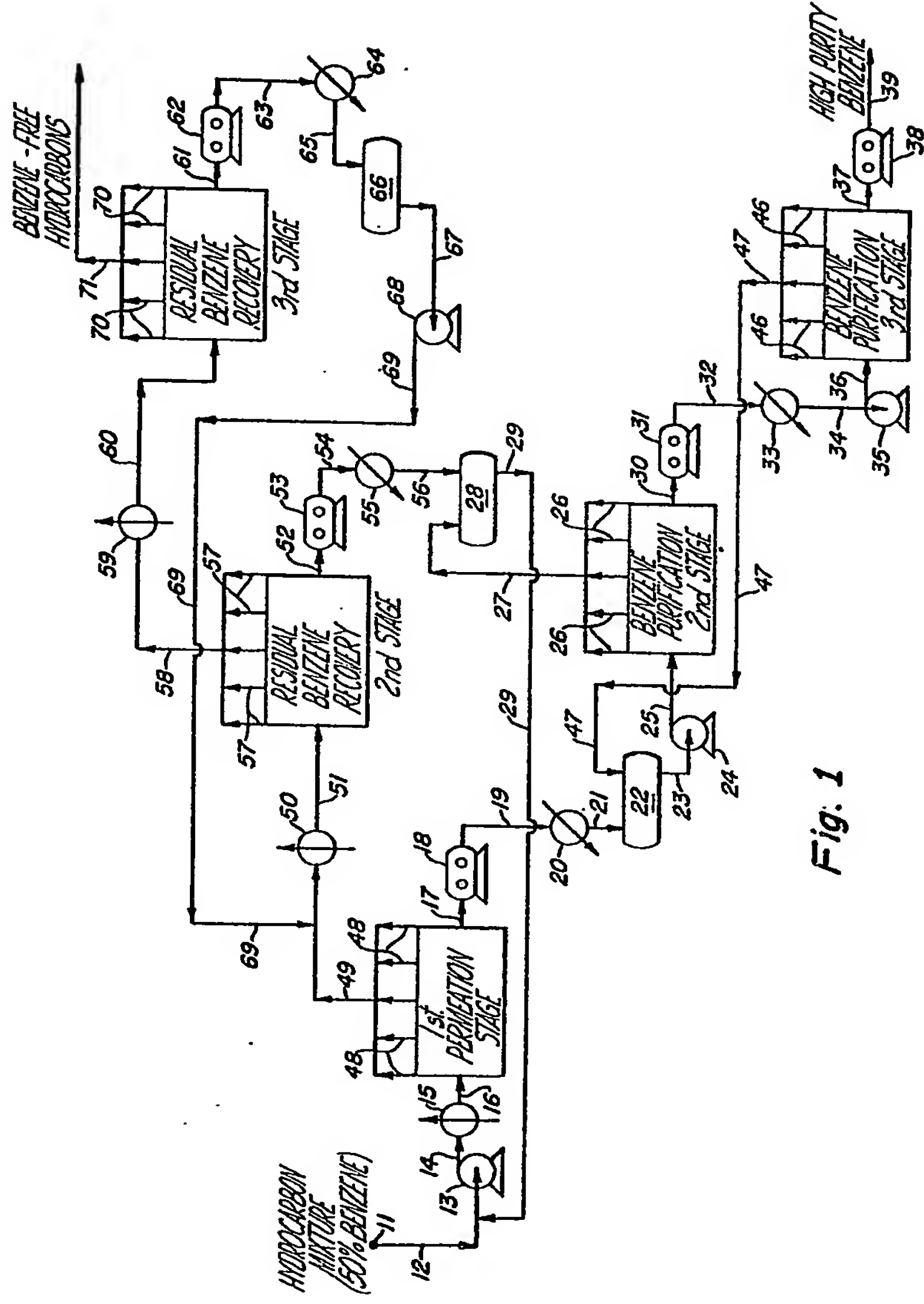
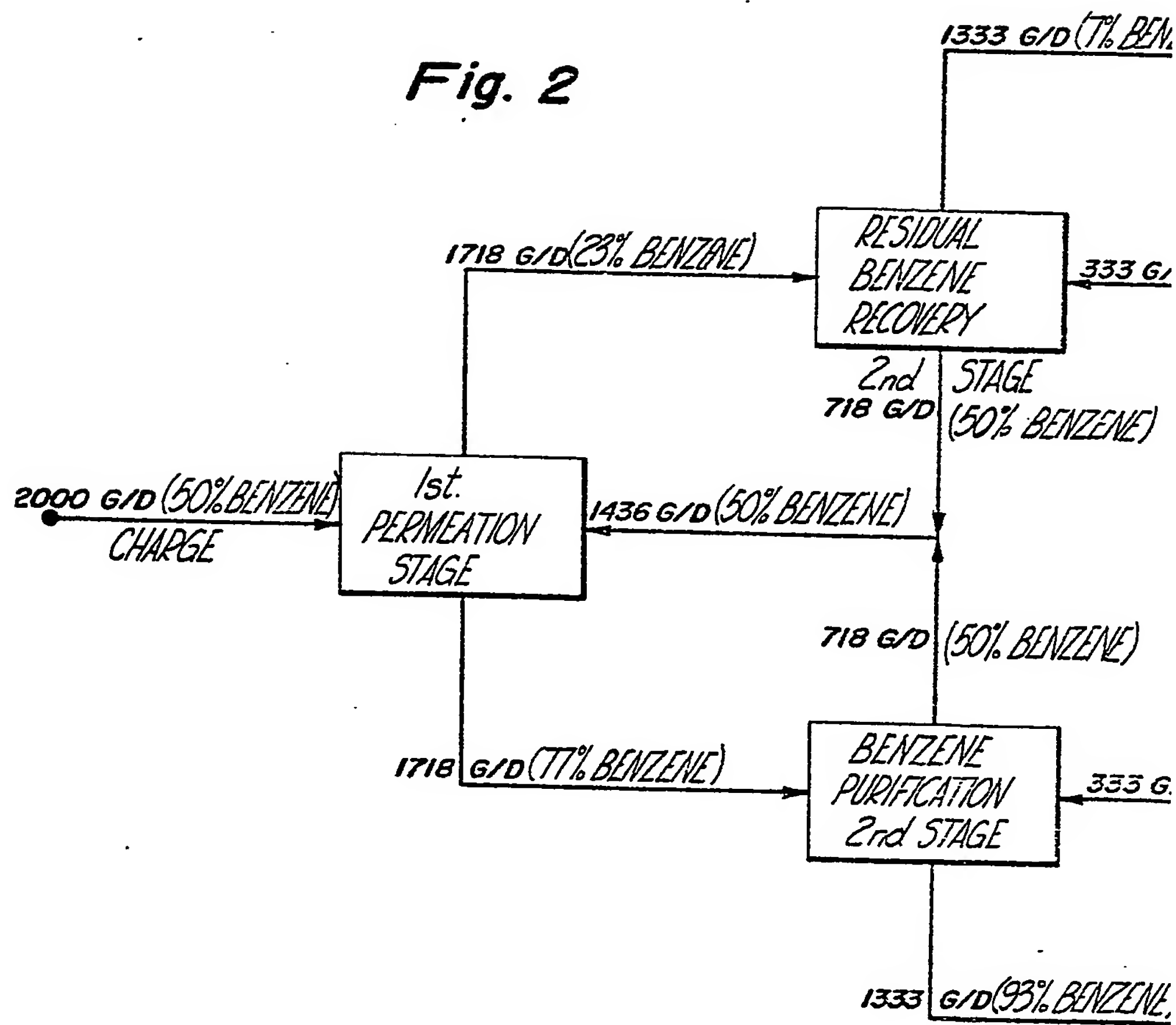


Fig. 1

Fig. 2



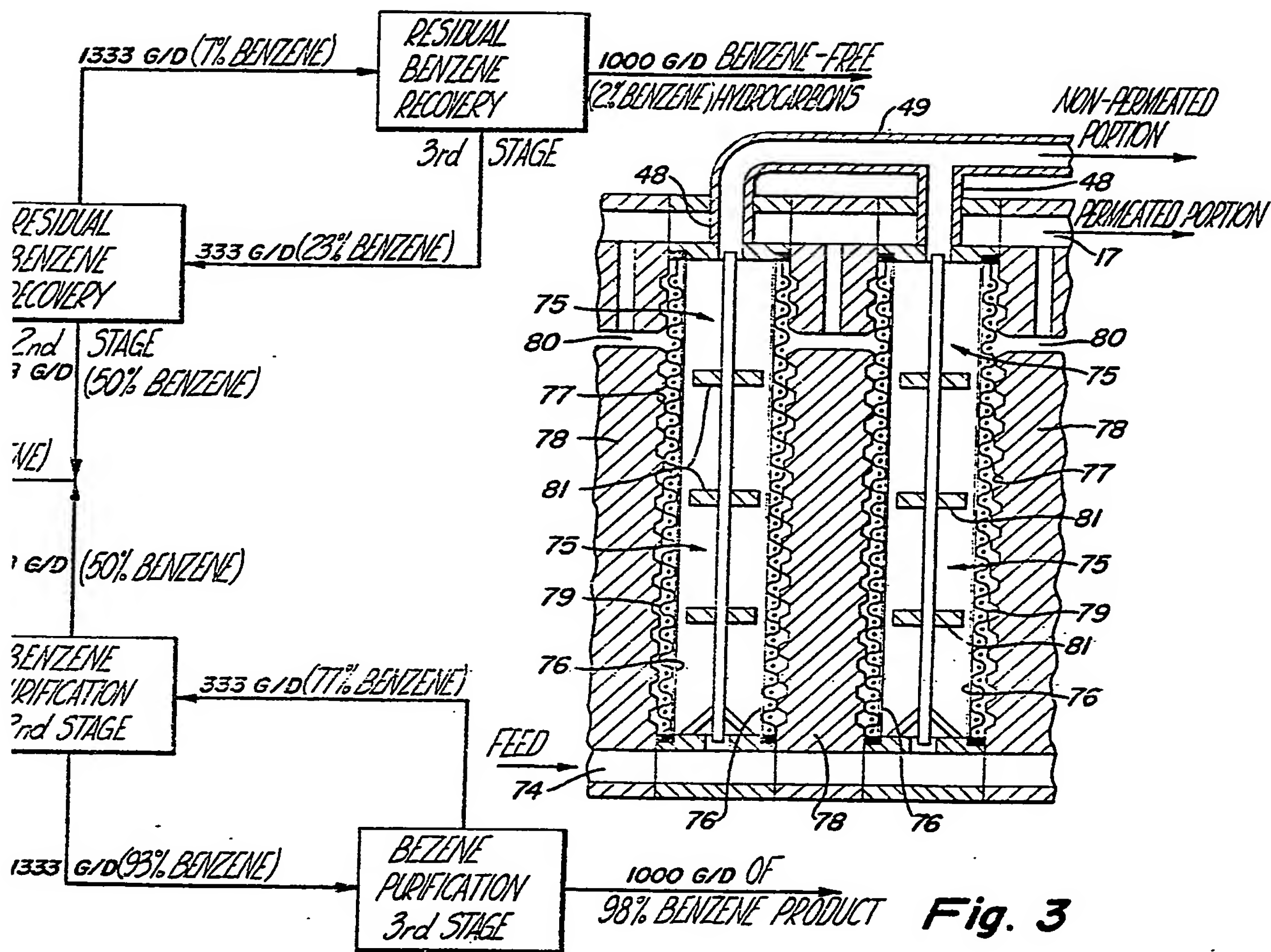


Fig. 3

Fig. 2

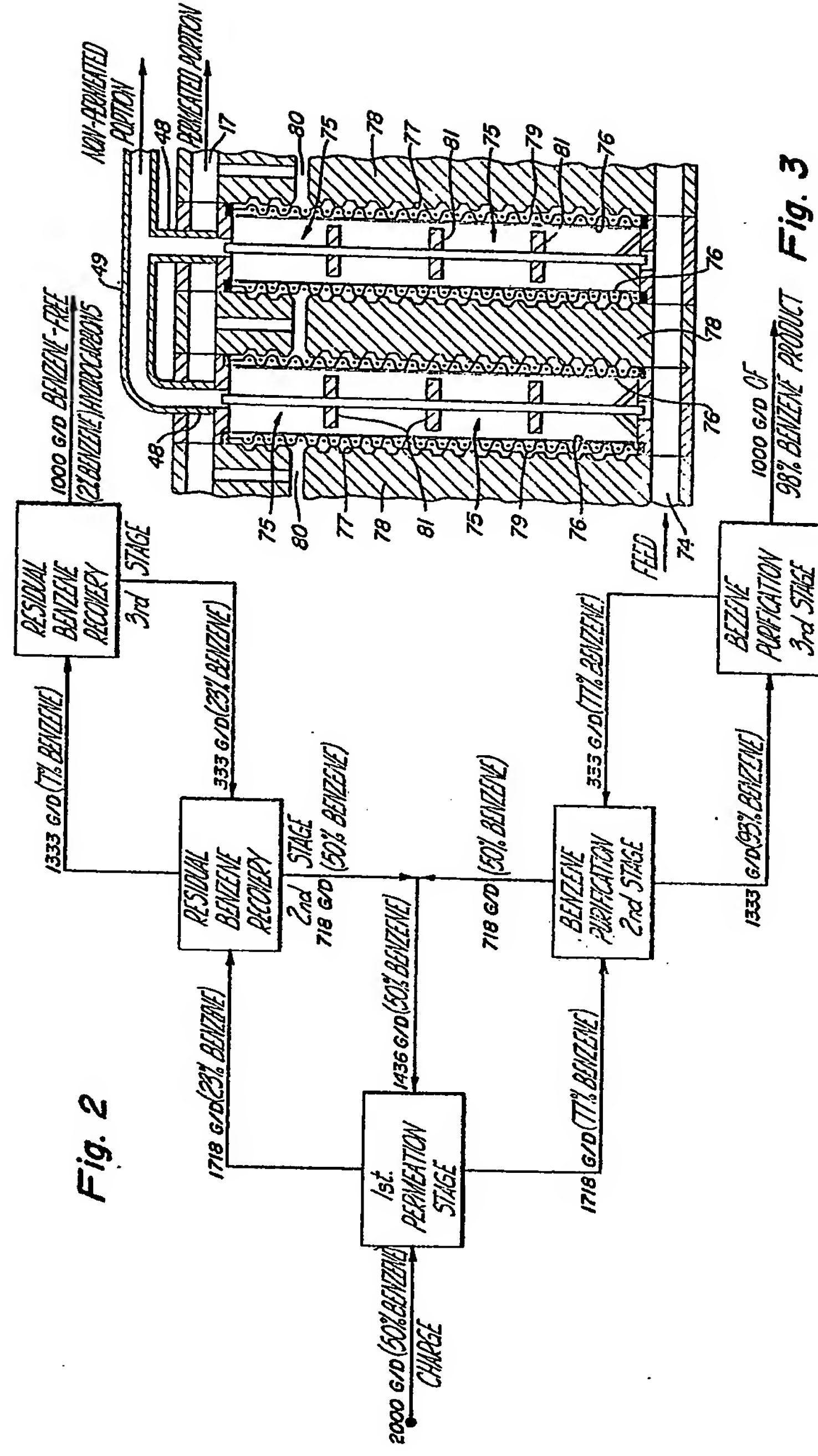


Fig. 3